

Hybrid density functional study of electronic and optical properties of phase change memory material: $\text{Ge}_2\text{Sb}_2\text{Te}_5$

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In this article, we use hybrid density functional (HSE06) to study the crystal and electronic structures and optical properties of well known phase change memory material $\text{Ge}_2\text{Sb}_2\text{Te}_5$. We calculate the structural parameters, band gaps and dielectric functions of three stable structures of this material. We also analyze the electron charge distribution using the Bader's theory of charge analysis. We find that hybrid density functional slightly overestimate the value of 'C' parameter. However, overall, our results calculated with the use of hybrid density functional (HSE06) are very close to available experimental values than calculated with the use of PBE functional. Specifically, the electronic band gap values of this material calculated with HSE06 are in good agreement with the available experimental data in the literature. Furthermore, we perform the charge analysis and find that naive ionic model fails to explain the charge distribution between the constituent atoms, showing the complex nature of this compound.

I. INTRODUCTION

$\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) chalcogenides have been of technological importance due to their applications for rewritable data-storage devices such as compact-disk (CD) and digital versatile disk (DVD). The underlying principle behind the data-storage process is based on the fast and reversible phase transformation between a crystalline phase and an amorphous phase, leading to changes in electrical conductivity and optical reflectivity [1–3]. In particular, the phase change happens at relatively low temperature range [4–6], making it feasible for phase change random access memory (PCRAM). More physical understanding of both amorphous and crystalline GST have been essentially needed since it could guide us to further enhancement.

The GST crystalline phase consists of two states namely metastable phase and stable phase. Based on high-resolution electron microscopy analysis, the metastable phase has been proposed to crystallize in the rocksalt-type structure($\text{Fm}\bar{3}\text{m}$) that Te atoms completely occupy the 4(a) site and Ge, Sb, and intrinsic vacancies randomly atoms completely occupy the 4(b) site[7]. On the other hand, the stable phase crystallizes in the hexagonal structure. Three different atomic arrangements have been proposed. I. I. Petrov *et al.* [8] firstly performed an experiment by using electron transmission microscope and they reported that GST is the hexagonal structure with space group $\text{P}\bar{3}\text{m}1$ having corresponding lattice constants $a = 4.20 \text{ \AA}$ and $c = 16.96 \text{ \AA}$, respectively. Te atoms occupy 1(a), 2(d), and 2(d) sites while Sb and Ge atoms occupy 2(d) and 2(c) sites. Later, B. J. J. Kooi *et al.*[9] argued that Ge atoms occupy 2(d) sites and Sb atoms occupy 2(c) sites. However, T. Matsunaga *et al.*[10] further investigated this by x-ray diffraction and they found different results. According to them, GST crystallizes in hexagonal structure with the space group $\text{P}\bar{3}\text{m}1$ and the lattice parameters $a = 4.2247 \text{ \AA}$ and $c = 17.2391 \text{ \AA}$. They have also indicated that Ge and Sb atoms randomly occupy 2(d) and 2(c) sites. Up to now, complete explanations of atomic arrangement of the GST stable phase has remained unclear. However, B. S. Lee and co-workers [6] and J. W. Park *et al.* [11] experimentally studied the electronic and optical properties of the stable GST phase. In addition, there are also theoretical investigations related to the stable GST phase. Z. Sun *et al.*[12] carried out first-principles electronic structure calculations based on the density functional theory(DFT) to compare three proposed models and they have concluded that the configuration proposed by Kooi *et al.*[9] is the most stable one.

Hybrid functional of J. H. Heyd, G. E. Scuseria and M. Ernzerhof, better called HSE06 [13] has been shown to give improved structural parameters for a number of systems as compared to the local density approximations (LDA) and Generalized gradient approximation (GGA) [14, 15].

In addition, they also provide improved band gaps which are close to experiment, slightly lower for most cases [14, 15]. Up to now, no theoretical studies have been conducted to investigate the structural and optical properties of GST material by using hybrid density functionals. In this work, we therefore perform the calculations to address structural and electronic properties of stable GST using GGA and hybrid density functional (HSE06). The optimized structural parameters and electronic structures are presented. Finally, the optical properties of this compound are also investigated.

II. METHODS/COMPUTATIONAL DETAILS

Ab-initio total energy calculations based on the density functional theory(DFT)[16] and all-electron projector-augmented wave method[17] have been performed by using the VIENNA AB INITIO SIMULATION PACKAGE (VASP)[18, 19]. The atomic structures were constructed according to the experimental data provided by refs. [8–10]. The generalized gradient approximation of Perdew Burke-Ernzerhof (PBE)[20] was employed as exchange-correlation functionals. 14 electrons ($3d^{10}4s^24p^2$) of Ge, 5 electrons ($5s^25p^3$) of Sb, and 6 electron ($5s^25p^4$) of Te were treated as valence electrons in the pseudopotentials. The cutoff energy for plane wave basis of 800 eV and the k-point mesh for brillouin zone integration of $8 \times 8 \times 2$ were used since they provide sufficient convergence in total energy of structural optimization. On the other hand, the denser k-point mesh of $16 \times 16 \times 8$ was adopted for calculating density of states(DOS) and dielectric functions.

Calculations using hybrid density functional (HSE06)[13] were also comparatively carried out. In this particular case, the exchange-correlation functionals are the rational mixing between the Fock exchange, PBE exchange and PBE correlation

$$E_{xc}^{HSE} = 1/4 E_x^{HF,SR}(\mu) + 3/4 E_x^{PBE,SR}(\mu) + E_x^{PBE,LR}(\mu) + E_c^{PBE}, \quad (1)$$

The PBE exchange term is decomposed into two parts namely short range (sr) and long-range (lr) while the correlation part is totally from PBE. The parameter μ represents the range when the short range term is negligible and it is 0.207^{-1} for HSE06. The detailed mathematical derivations and tests of HSE06 functionals are given in ref. [13]. In order to obtain satisfactory results with reasonable computing time, the lower cutoff energy and k-point mesh, 600 eV and $4 \times 4 \times 2$, respectively were used for structural optimization. The denser k-point mesh was adjusted higher to be $8 \times 8 \times 2$ for calculating DOS and dielectric functions. The conjugate gradient scheme utilized for electronic relaxation algorithm is applied to all the structural optimization. The volume, shape, and

atomic positions were fully optimized and relaxations were allowed until the Hellmann-Feynman forces on the atoms were less than 0.005 eV/\AA . In addition, the calculated electronic charge density from the optimized atomic structure was used to calculate electronic charge partitioned for each atom by using a grid-based Bader charge analysis [21, 22]. The zero flux surface of the electronic charge density is used to determine the amount of charge occupied by that particular atom.

III. RESULTS AND DISCUSSION

We start our calculations by optimizing atomic structures of the stable phase of GST proposed in references [8–10] and they are labeled as A (I. I. Petrov *et al.*[8]), B (B. J. Kooi *et al.*[9]), and C (T. Matsunaga *et al.* [10]), respectively. The equilibrium geometries by using PBE and HSE06 functionals are given in 1. It can be seen that the unit cell (1 formula unit) consists of 9 atoms (2 Ge, 2 Sb and 5 Te). The stable GST is a layered structure that Ge, Sb, and Te atoms are stacked along c -axis (in the $[0001]$ direction). The optimized lattice parameters are listed in I. PBE functionals obviously overestimate lattice parameters with the maximum 2 % difference as compared to the reported experimental values. This comes from the well-known deficiency that GGA functionals overestimate lattice constants. However, we have found that our calculations are in good agreement with those previously reported calculations as also indicated in I. However, using the HSE06 functional, the lattice constant a is improved to be closer to the experimental values, but the lattice constant c is overestimated. This could be related to that the stable GST is a layered structure along c -axis. The interactions between adjacent layers are probably low and hybrid functional may fail to explain these weak interactions.

After acquiring the complete information about structural parameters, we proceed to investigate the corresponding electronic structures of these stable phases of $\text{Ge}_2\text{Sb}_2\text{Te}_5$. Our calculated density of states (DOS) with the use of PBE and HSE06 functionals of these stable phases are shown in 2. We see that PBE and HSE06 give almost similar DOS and it is found that Te-derived states are mainly formed at the top of the valence band while Ge, Sb, and Te share the bottom of conduction band. However, there is strong hybridization of Sb and Te atoms in the conduction band around 0.5-1.0 eV for A and C whereas Ge, Sb, and Te atoms almost equally hybridize for B. This can be explained by their different atomic arrangements. For A, Sb atoms from 2(d) sites are surrounded by Te atoms from 1(a), 2(d), and 2(d) sites. For B, Sb atoms from 2(c) site are surrounded by Te atoms from 1(a) site. In addition, states in the conduction band have very similar shapes but they are pushed upward, resulting in higher band gaps as indicated in II. PBE functional predicts band

gaps as 0.00 eV, 0.24 eV, and 0.22 eV for A, B, and C, respectively while it has been reported that stable GST has the band gap ranging from 0.50-0.57 eV[6, 11]. The band gaps are quantitatively underestimated because of the main deficiency of DFT to deal with excitation. However, HSE06 hybrid functional gives band gaps closer to the experimental values found in the literature. The C phase has the band band gap of 0.48 eV which is in good agreement with the experimental values while B phase has slightly lower, 0.37 eV. On the other hand, the phase A has the smallest band gap of 0.26 eV.

In 3, we show the real and imaginary parts of dielectric functions of $\text{Ge}_2\text{Sb}_2\text{Te}_5$. The left side represents the dielectric functions calculated by using PBE functional whereas the right side denotes those calculated by using hybrid density functional. For PBE functional, A and C have nearly similar dielectric functions. They have the same amplitude of the real part dielectric function at zero energy and their main peaks of the imaginary part are located between 1.5-2.0 eV, in good agreement with reported results in ref. [11]. However, the main peak of the imaginary part of B is slightly lower than A and C. It has been experimentally reported that the imaginary dielectric function locates at 1.5 eV[11]. For HSE06 functional, It is found that A, B, and C, have slightly different dielectric functions considering in terms of the locations of main peaks of the imaginary part, the starting point at zero energy of the real part and the amplitudes.

We have also calculated the electronic charge distribution by using Bader Charge analysis[21, 22] and list our results in III. As mentioned earlier that Ge, Sb, and Te have 14, 5, and 6 valence electrons, respectively. In a pure ionic model, Ge and Sb would loose 4 and 3 electrons respectively and Te may gain ≈ 3 electrons. But in our case the situation is rather complex. For instance in phase A, Ge and Sb are loosing only 0.31 and 0.6 electrons respectively, which are gained by Te. These results represent the complex nature of this material and reveal the importance of quantitative analysis over a simple ionic model. In the three proposed stable phases of this material, the charge distribution is almost same. Although, the values obtained for B phase favors slightly the charge transfer from Ge and Sb to Te, but the numbers are not fundamentally different from those, which were calculated for A and C structures.

IV. CONCLUSIONS

In summary, we have performed comparative study of the structural, electronic and optical properties of the stable structures of $\text{Ge}_2\text{Sb}_2\text{Te}_5$, with the use of GGA and hybrid density (HSE06) functionals. In our present study, we have shown that structural parameters and electronic band

gap of this material calculated with the use of hybrid density functional (HSE06) are in good agreement with the available experimental results than calculated with the use of PBE functional. However, HSE06 functional slightly overestimate the C parameter and optical properties of this compound. We have also analyzed the charge distribution between the constituent elements of this material using the Bader's theory of atoms and we find that, due to the complex nature of this compound, the simple ionic model fails to explain it. We have shown that, on the overall, hybrid density functional (HSE06) is important for the correct description of GST material and especially to reproduce the electronic structure of this compound. Finally, we have presented that all the calculated parameters of stable phase B of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ are more closer to available experimental data than stable phases A and C.

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Table I. The calculated structural parameters of the stable $\text{Ge}_2\text{Sb}_2\text{Te}_5$ phase.

Proposed structures	xc -functionals	a_0 (Å)	c_0 (Å)
A	PBE	4.263	17.971
	PBE ^e	4.270	17.720
	HSE06	4.216	17.832
	Experiment ^a	4.200	16.960
B	PBE	4.300	17.237
	PBE ^e	4.290	17.250
	HSE06	4.230	18.058
	Experiment ^b	4.200	16.960
C	PBE	4.278	17.743
	PBE ^d	4.270	17.890
	HSE06	4.204	18.196
	Experiment ^c	4.220	17.240

^aExperiment in Ref. [8].^bExperiment in Ref. [9].^cExperiment in Ref. [10].^dDFT calculations in Ref. [11].^eDFT calculations in Ref. [23].Table II. The calculated band gap energies of the stable $\text{Ge}_2\text{Sb}_2\text{Te}_5$ phase.

Proposed structures	PBE (eV)	HSE06 (eV)
A	0.00	0.26
B	0.24	0.37
C	0.22	0.48
Experiments	0.57 (Ref. [11]), 0.50 (Refs. [6])	

Table III. The calculated electronic charges of the stable $\text{Ge}_2\text{Sb}_2\text{Te}_5$ structures by Bader charge analysis.

atomic species	electronic charge (e)		
	A	B	C
Ge(1)	13.69	13.60	13.66
Ge(2)	13.69	13.60	13.66
Sb(1)	4.40	4.35	4.40
Sb(2)	4.40	4.35	4.40
Te(1)	6.52	6.44	6.49
Te(2)	6.29	6.37	6.32
Te(3)	6.29	6.37	6.32
Te(4)	6.36	6.46	6.37
Te(5)	6.36	6.46	6.37

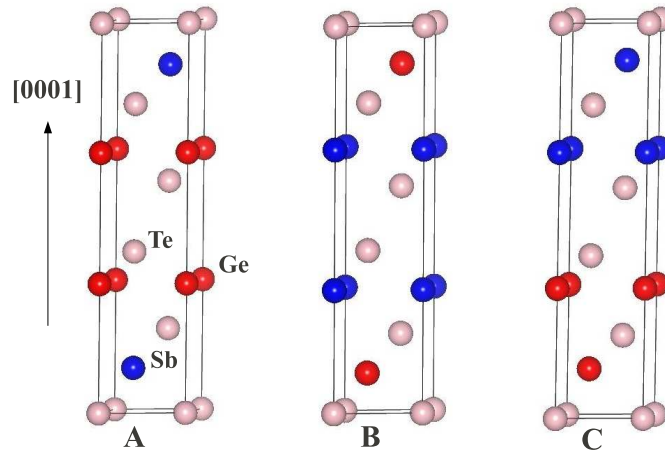


Figure 1. The optimized atomic structures of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ proposed by (A) I. I. Petrov *et al.*[8], (B) B. J. Kooi *et al.*[9] and (C) T. Matsunaga *et al.*[10]. Red, blue, and pink spheres represent Ge, Sb and Te atoms, respectively.

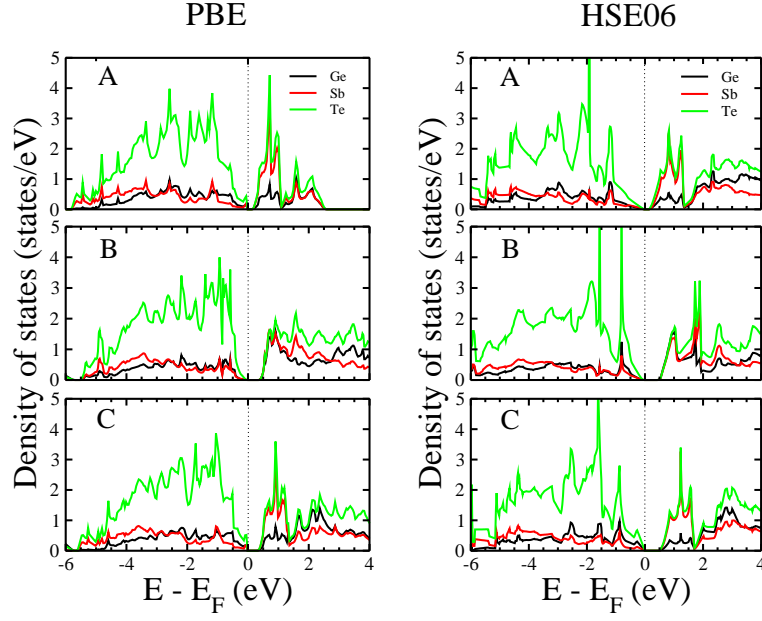


Figure 2. Density of states (DOS) of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ calculated with PBE (left side) and HSE06 (right side). The fermi level is shifted to zero.

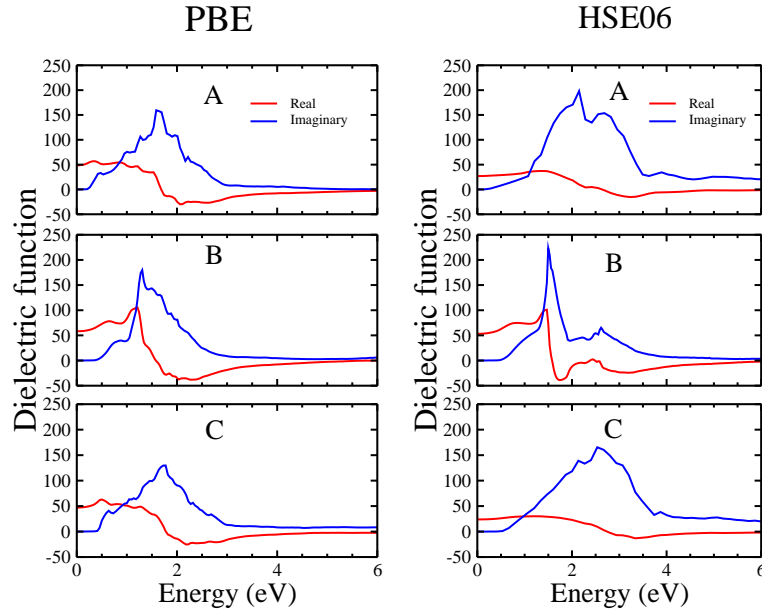


Figure 3. The real and imaginary parts of dielectric functions of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ calculated with PBE (left side) and HSE06 (right side).